RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 18 1 NOVEMBER 1991-II

Heat-capacity investigations near the normal-superconducting transition of $YBa_2Cu_3O_7$

B. Zhou, J. Buan, and C. C. Huang
Center for the Science and Application of Superconductivity and School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

J. V. Waszczak and L. F. Schneemeyer
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 20 May 1991; revised manuscript received 8 July 1991)

A high-resolution ac quasiadiabatic calorimeter has been employed to measure the heat-capacity anomaly associated with the normal-superconducting transition of several slightly twinned $YBa_2Cu_3O_7$ single-crystal samples. The heat-capacity anomaly from one of the samples displays a very sharp 10%–90% jump on the high-temperature side of anomaly and can be described by a mean-field model based on the BCS theory.

Since the discovery of high-temperature-superconducting behavior in compounds containing cuprate, there has been considerable experimental effort aimed at studying the thermal properties in the vicinity of the normal-superconducting transition temperature (T_c).[1-4] One important feature that the high-T_c superconducting materials possess is that the low-temperature coherence length (ξ_0) is only on the order of the lattice spacings (approximately 10 Å). This is much smaller than ξ_0 of conventional superconducting materials (typically fifty to a few thousand angstroms). Because of this extremely short coherence length among the high-T_c materials, by virtue of the Ginzburg criterion, one expects that the critical fluctuation region, which is extremely small among the conventional superconductors (less than 10^{-6} in reduced temperature), may become experimentally accessible among the high-T_c superconducting materials.[5,6] Recent experimental investigations on untwinned $YBa_2Cu_3O_7$ samples and polycrystalline samples give noticeably pronounced heat-capacity anomalies in the immediate vicinity of T_c which have been accounted for by the Gaussian fluctuations.[1-3] Here we will report our heat-capacity measurements from several slightly twinned $YBa_2Cu_3O_7$ single crystals. Unlike the results reported by Inderhees and co-workers[1,2] and Schnelle *et al.*,[3] we do not observe any additional heat-capacity anomaly other than the mean-field heat-capacity jump. Although the magnitude of our heat-capacity anomalies are smaller than the most recent data reported by Inderhees *et al.*,[2] they are comparable to their previous results.[1] In addition, the widths between 10% and 90% of the heat-capacity jump on the high-temperature side of the heat-capacity anomaly are used to compare the sharpness of the transitions. In this respect, the results from one of our samples displaying the sharpest transition width will be reported here.

Heat-capacity measurements were performed on three slightly twinned single-crystal samples of $YBa_2Cu_3O_7$ with different sizes. The results from one of them with nominal dimension $2.0\times1.0\times0.03$ mm^3 will be reported here. The sample preparation (from a Cu-O flux) and characterization of the samples have been reported elsewhere.[7] Because of large phononic and electronic (normal electrons) contributions to the heat capacity, the heat-capacity anomaly associated with the normal-superconducting transition is relatively small. The quasiadiabatic ac calorimetric technique[8] was employed to measure the temperature variation of heat capacity. Using an extremely small amount of GE varnish, the sample was attached to a tiny crossed chromel-constantan thermocouple junction (thermocouple wires were 13 μm in diameter) with four leads. The thermocouple wires were attached to a ring made of fiberglass plate to secure the orientation of the sample. The other side of the sample was coated with aquadag to enhance the radiation absorption and eliminate the possible change in absorption coefficient through the transition temperature. Mechanically chopped radiation from a tungsten lamp served as the ac heating source. A mask was used to shield the surrounding and insure that only the sample was heated by the chopped radiation. The weak thermal link between the sample and the reservoir is provided by helium gas at a pressure of 0.5 atm. The average sample temperature was measured through one pair of chromel-constantan thermocouple junction leads with an ice bath as the reference junction. The other pair of thermocouple junction leads was used to obtain the magnitude of the temperature oscillation produced by the ac heating source. This signal is inversely proportional to the measured heat capacity and it is detected by a phase sensitive lock-in amplifier after being amplified by a low-impedance transformer. A personal computer is employed to acquire the data and convert them into sample temperature and heat capacity. To determine the appropriate operating frequency, the frequency response curve[9] was obtained by measuring the magnitude of temperature oscillation as a function of chopping frequency with the sample temperature held at 85 K. The area probed by the thermocouple junction is directly related to the thermal diffusion length, $l=(D/\pi f)^{1/2}$. Here f and D are operating frequency and thermal diffusivity of the sample, respectively. In principle, one can choose an extremely high chopping frequency to reduce the probing area so that the rounding effect due to sample inhomogeneities can be minimized. However, there exists, at least, one limitation. The operating frequency should be smaller than the high

RAPID COMMUNICATIONS

cutoff frequency (f_h) (greater than 320 Hz for our sample). This condition ensures that the sample as a whole is close to thermal equilibrium during each heating cycle. We chose a chopping frequency $f = 78$ Hz which is also much larger than the lower cutoff frequency (f_l) (smaller than 10 Hz). This second condition ensures quasiadiabatic condition of the calorimeter. Under the condition that $f_h \gg f \gg f_l$, the sample heat capacity (C) is related to the magnitude of the temperature oscillation (ΔT) measured by the tiny thermocouple junction through the following relation:

$$C = P_A / 2\pi f \Delta T .$$

Here P_A is the input power per unit area. Its value is calibrated by measuring the heat capacity of a cover glass slide coated with aquadag with known heat capacity[9] at room temperature. With our operating frequency of 78 Hz and using the reported thermal-conductivity data,[10] we found the sample thermal diffusion length to be $l = 0.06$ mm in the vicinity of the normal-superconducting transition temperature ($T_c = 92$ K).

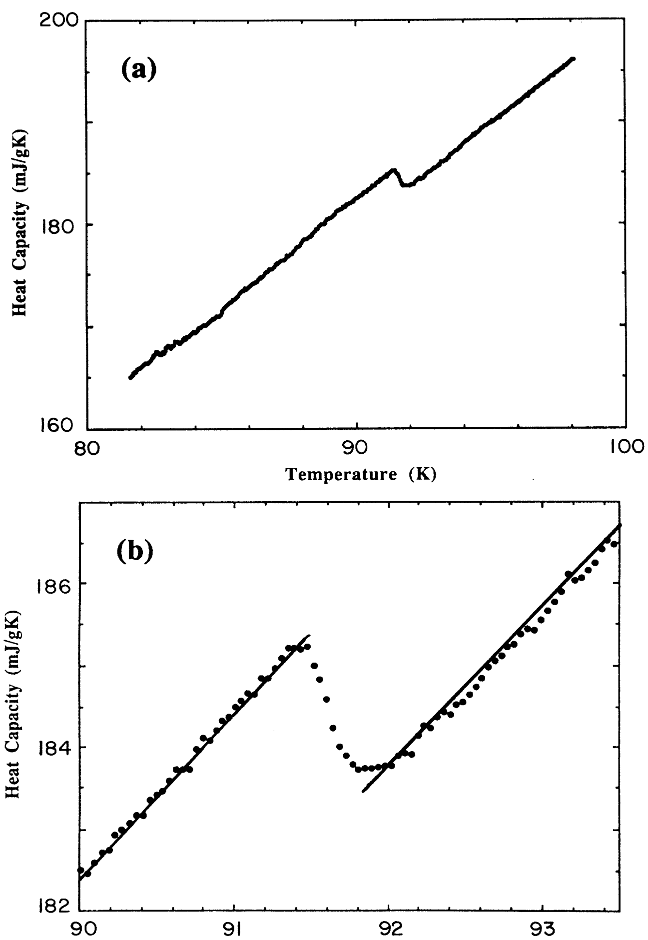

FIG. 1. (a) Heat capacity of $YBa_2Cu_3O_7$ vs temperature in the range from 82 to 98 K. (b) Temperature dependence of heat capacity in the immediate vicinity of T_c ($= 91.625$ K). The solid lines indicate the fitting results to the mean-field expression over the entire temperature range (82–98 K).

The measured heat-capacity data as a function of temperature are displayed in Fig. 1(a) as solid dots. The same set of heat capacity data over a narrow temperature window near T_c is shown in Fig. 1(b). As one can see, the heat capacity data for both $T > T_c$ and $T < T_c$ regions are linear functions of temperature. The width in temperature (ΔT_w) between 10% and 90% of the heat-capacity jump of our data is about 0.22 K. For comparison, Table I lists the results from previously published data.[1–4] The salient feature of this comparison is that the width (ΔT_w) of our sample is almost a factor of 2 smaller than the best previously published result.

The solid line in Fig. 1 is the best fitting result to the following heat-capacity expression based on the BCS model:[11]

$$C_p = \begin{cases} A + BT, & T > T_c, \\ A + BT + aT(1 + bt), & T < T_c. \end{cases} \tag{1}$$

Here $A + BT$ is the background heat-capacity contribution from phonon, normal electron, etc. The $aT(1+bt)$ term with $b = 1.72$ is the mean-field heat-capacity contribution below T_c according to the BCS theory.[11] The reduced temperature $t = (T - T_c)/T_c$. Within the experimental resolution, Eq. (1) with A, B, a, and T_c as fitting parameters gives us very good description of all our experimental data shown in Fig. 1(a). The best fitting result leads to $A = -1.95$ mJ/g K, $B = 2.02$ mJ/g K^2, $a = 3.00 \times 10^{-2}$ mJ/g K^2, and $T_c = 91.625$ K. The heat-capacity jump at T_c ($\Delta C = 2.75$ mJ/g K^2) is comparable to the previously reported results.[1]

We have also tried to fit our entire set of data to the following expression including contributions due to Gaussian fluctuations,[12]

$$C_p = \begin{cases} A + BT + C^+ |t|^{-(2-d/2)}, & T > T_c, \\ A + BT + aT(1+bt) + C^- |t|^{-(2-d/2)}, & T < T_c. \end{cases}$$

Here d is the dimensionality of the system. Even with two additional fitting parameters (C^+ and C^-, the amplitude of the Gaussian heat-capacity anomaly above and below T_c), no improvement in the fit was obtained. Furthermore, we consistently found $C^+ > 0$ and $C^- < 0$ which are physically unacceptable. Also the fitted values of

TABLE I. Summary of heat-capacity data from various research groups.

Sample	Width (mK) of the heat-capacity anomaly[a]	Ref.
A	450	2
B	490	1(b)
C	> 800	1(a)
D	740	3(a)
E	430	3(b)
F	220	this work

[a]This is the 10%–90% width of the heat-capacity jump on the high-temperature side of the heat-capacity anomaly.

$C^+(4\times10^{-5}$ mJ/gK) and $C^-(-6\times10^{-5}$ mJ/gK) are much smaller than these coefficients [$C^+(=2\times10^{-1}$ mJ/gK) and $C^-(=3\times10^{-1}$ mJ/gK)] being predicted in Gaussian approximation for $n=2$ and $d=3$. In the case of $n=2$ and $d=2$, the calculated coefficients $C^+=C^-(=7\times10^{-2}$ mJ/gK) again are much larger than our fitted values.

The other single-crystal samples give similar heat-capacity anomalies with a smaller heat-capacity jump and/or larger transition width (ΔT_w). However, the fits also favor the mean-field model without the Gaussian fluctuation term.

The data shown in Fig. 1 display a slight asymmetry with respect to mean-field fitting results. We believe that this is mainly due to the nonuniform T_c distribution caused by impurity and/or defect gradient throughout our probing area (approximately 60 μm in diameter). Experimental investigations of the relation between the size of probing area and the magnitude of ΔT_w or the overall asymmetry of the heat-capacity anomaly near T_c are in progress. By employing ac quasiadiabatic calorimetric measurements on a thin slab of sample, the probing area is inversely proportional to the oscillating frequency (f) of the ac power input provided that the conditions $f_h \gg f \gg f_l$ are satisfied.

Because the reduced Ginzburg temperature t_G is inversely proportional to $(\Delta C)^2(\xi_0)^6$, a smaller value in ΔC, in principle, should lead to a larger value in t_G. However, the fact that our sample with the sharpest transition width and a smaller value in ΔC fails to show any additional heat-capacity contribution other than that attributable to the simple mean-field model is puzzling. During the course of our calorimetric investigations of phase transitions between various mesophases in liquid crystals, we have faced a similar question. According to x-ray diffraction studies, both the nematic–smectic-A and smectic-A–smectic-C transition have an effective bare correlation length $\xi_0=[\xi_\parallel(\xi_\perp)^2]^{1/3}$ which is roughly the cubic root of the effective volume occupied by each liquid-crystal molecule.[13] The nematic–smectic-A transition has been well established to be fluctuation dominant.[14] Whether the smectic-A–smectic-C transition is mean-field or critical was not resolved until detailed heat-capacity studies on this transition demonstrated that it is definitely mean-field-like.[15] This therefore constitutes one example in which the magnitude of the bare correlation length (ξ_0) alone is not sufficient to predict the crossover from the mean-field region to the fluctuation dominant region. Further investigations on other superconducting samples are in progress.

The authors would like to acknowledge many useful discussions with A. Goldman and help from T. Stoebe. This work is partially supported by the Graduate School, University of Minnesota, by the Material Research Group Program of the NSF under Grant No. DMR-89-08094 and by the Department of Administration of the State of Minnesota.

[1](a) S. E. Inderhees, M. B. Salamon, N. Goldenfeld, J. P. Rice, B. G. Pazol, and D. M. Ginsberg, Phys. Rev. Lett. **60**, 1178 (1988); (b) M. B. Salamon, S. E. Inderhees, J. P. Rice, B. G. Pazol, D. M. Ginsberg, and N. Goldenfeld, Phys. Rev. B **38**, 885 (1988).

[2]S. E. Inderhees, M. B. Salamon, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett. **66**, 232 (1991).

[3](a) N. E. Phillips, R. A. Fisher, J. E. Gordon, S. Kim, A. M. Stacy, M. K. Crawford, and E. M. McCarron, Phys. Rev. Lett. **65**, 357 (1990); (b) W. Schnelle, E. Braun, H. Broicher, R. Domel, S. Ruppel, W. Braunisch, J. Harnischmacher, and D. Wohlleben, Physica C **168**, 465 (1990).

[4]K. Kitazawa, T. Atake, H. Ishii, H. Sato, H. Takagi, S. Uchida, Y. Saito, K. Fueki, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L748 (1987).

[5]C. J. Lobb, Phys. Rev. B **36**, 3930 (1987).

[6]A. Kapitulnik, M. R. Beasley, C. Castellani, and C. Di Castro, Phys. Rev. B **37**, 537 (1988).

[7]L. F. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature (London) **328**, 601 (1987).

[8]P. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1968).

[9]C. C. Huang, J. M. Viner, and J. C. Novack, Rev. Sci. Instrum. **56**, 1390 (1985).

[10]J. Heremans, D. T. Morelli, G. W. Smith, and S. C. Strite III, Phys. Rev. B **37**, 1604 (1988).

[11]A. A. Abrikosov, L. P. Gorkov, and I.E. Dzyaloshinski, *Method of Quantum Field Theory in Statistical Physics* (Dover, New York, 1963), p. 306; von B. Muhlschlegel, Z. Phys. **155**, 313 (1959). The coefficient b is determined from a linear fitting to the tabulated heat-capacity data with $0.88 \le t \le 1.0$ which is the fitting range of our experimental data.

[12]S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1976).

[13]Due to the anisotropy of liquid-crystal molecules, usually the correlation lengths along ($\xi_\parallel$) and perpendicular to ($\xi_\perp$) the long axis of the molecule are different from each other.

[14]C. A. Schantz and D. L. Johnson, Phys. Rev. A **17**, 1504 (1978); C. W. Garland, G. B. Kasting, and K. J. Lushington, Phys. Rev. Lett. **43**, 1420 (1979).

[15]C. C. Huang and J. M. Viner, Phys. Rev. A **25**, 3385 (1981); R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. Goodby, Phys. Rev. A **27**, 1251 (1983).